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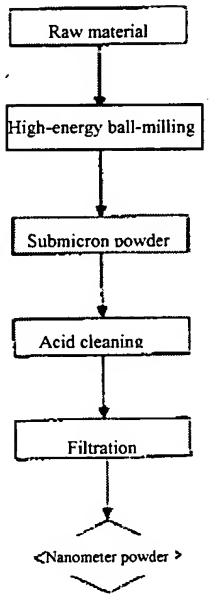
(54) Title of Invention: Method for preparation of titanium diboride nanometer powder

(57) Abstract:

This invention involves the method for preparation of titanium diboride nanometer powder. The invention first performs ball-milling on titanium diboride powder with average particle diameter of 5 microns, so as to provide the particle surface with a certain degree of activation energy and intracrystalline imperfection to get titanium diboride powder at submicron grade with uneven particle diameter; then, the powder goes through secondary thinning and homogenizing treatment in acid solution, and after cleanup acid treatment, titanium diboride nanometer powder can be obtained with average particle diameter at around 50 nanometers. The advantage of this invention lies in its use of simple technology and generation of powder in even particle diameter, and is suitable for preparation of powder on a large scale.



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Claims

1. This is a method for preparation of titanium diboride nanometer powder, and it has the following features: high-energy ball-milling is performed on TiB_2 powder with average particle diameter of 5 um, the ball and material ratio is 20 : 1, ball-milling goes on for 40 to 50 hours, and powder is obtained with particle diameter of 0.1 to 0.3 um, and such powder is placed in the acid solution prepared through mixing concentrated hydrochloric acid with water, or in the acid solution prepared through mixing concentrated nitric acid, concentrated phosphoric acid and water, which is agitated for 30 minutes first, then is settled for 10 minutes at room temperature, is washed with clean water 2 to 3 times, is filtered through suction, and is dried to get even TiB_2 powder with average particle diameter at around 50 nm.
2. With regard to the preparation method as mentioned in Claim 1, it has the following features: the compounding ratio of the acid solution used for acid washing is: the ratio between concentrated hydrochloric acid and water is 1 : 5 to 1 : 8, or the ratio among concentrated nitric acid, concentrated phosphoric acid and water is 1 : 1 : 3 to 1 : 1 : 5.

Description

Method for Preparation of Titanium Diboride Nanometer Powder

Field of Technology

This invention involves a method for preparation of nanometer powder.

Background Technology

Titanium diboride (TiB_2) ceramic powder is a type of important engineering ceramic raw material, with the characteristics of high melting point, high degree of hardness, high chemical stability as well as good heat conduction and electric conduction. It is mainly used in the following areas: rigid tool material, high temperature corrosion-resistant electrodes, large-scale integrated circuits using high-strength lead frame materials, and so on. The titanium diboride ceramic powder that is more often used currently is prepared through use of self-propagating high temperature synthesis technology, and the average particle diameter thereof is about 5 um. In order to further improve material features, it is necessary to prepare nanometer grade titanium boride powder. In 1995, Susan E. Bates at Washington University in the United States published a paper with the title "Synthesis of titanium boride nanocrystallites by solution-phase processing" in the *Journal of Material Research*, in which $NaBH_4$ and $TiCl_4$ are used as raw materials to react in trimethylbenzene solution at 164°C to get amorphous TiB_2 precursor powder, which is then annealed at 900 to 1100°C to produce TiB_2 nanometer powder with particle diameter ranging from 5 to 100 nm. Such preparation uses complicated technology, makes it difficult to control product components, and needs after-treatment, so that it is not easy to realize industrial production in large volume. In 1996, another paper written by R. L. Axelbam at Washington University was also published in the *Journal of Material Research* with the title "Gas-phase combustion synthesis of titanium boride nanocrystallites," which reports that $TiCl_4$, BCl_3 and Na are used as raw materials to produce TiB_2 nanometer powder with particle diameter less than 15 nm through gas phase combustion reaction in Na gas atmosphere. This technology can be used to produce TiB_2 nanometer powder in small particle diameter with high purity, but the technological content and cost it requires are both relatively high.

The current technologies for preparation of nanometer powder mainly include: chemical vapor phase process, chemical coprecipitation process, mechanical alloying, sol-gel method, spray cooling and fluidization method. The chemical vapor phase process has strict requirements on technological conditions, and is relatively high in cost; the chemical coprecipitation process requires selection of precursor that can dissolve in alkaline solution, which is more difficult for preparation of boride; the nanometer powder prepared through mechanical alloying is not even in particle diameter; the raw materials used in the sol-gel method are high in price, and the solvent is toxic, and at the same time, the performance of heat treatment under high temperature makes it easy for particles to conglobe quickly; the spray cooling requires high temperature and vacuum conditions, which put relatively high requirements on equipment and operation; the technological process and equipment for fluidization method are complicated, and the cost is high for preparation in large volume.

Content of Invention

The purpose for this invention is to make use of a relatively simple method to produce in large volume TiB_2 nanometer powder with even particle diameter.

The technical solutions used in this invention to resolve its technical issues are: (1) for micron grade TiB_2 powder, mechanochemistry process is used to perform primary thinning on crystal particles so that submicron grade powder is obtained with uneven particle size, and at the same time, a certain degree of lattice distortion is generated to activate particle surface; (2) thinning is further performed on crystal particles through cleanup acid treatment, and the layer structure and hydrogen pick-up property of boride are used to obtain nanometer TiB_2 powder with even particle diameter.

The specific process of implementation for this invention is described in detail below:

1. High-energy ball-milling is performed on TiB_2 powder with average particle diameter at 5 um and with purity above 98%, the ball and material ratio is 20 : 1, and ball-milling goes on for 40 to 50 hours. Powder is obtained with particle diameter at 0.1 to 0.3 um.
2. Acid solution prepared through mixing concentrated hydrochloric acid with water at the ratio of 1 : 5 to 1 : 8, or through mixing concentrated nitric acid, concentrated phosphoric acid and water at the ratio of 1 : 1 : 3 to 1 : 1 : 5. After ball-milling, the powder is placed in the abovementioned acid solution for agitation for 30 minutes, and after it has been placed at room temperature to settle for 10 minutes, water is used to wash it 2 to 3 times so as to remove the acidic materials from the surface of the precipitate, and then it is filtered through suction, and is dried to get even TiB_2 nanometer powder with average particle diameter at around 50 nm and with purity above 98%.

The advantage of this invention is: in comparison with other technologies for preparation of nanometer powder, this invention is simple in technological process, the particle diameter is even, and it is easy to prepare in large volume.

Specific Implementation Procedures

The attached figures are used below to introduce the specific implementation procedures of this invention in detail.

Figure 1: The engineering flow sheet for preparation of titanium diboride nanometer powder

Implementation Case 1: 100 grams of TiB_2 powder with average particle diameter at 5 microns is mixed with appropriate amount of absolute ethyl alcohol, and is placed in the high-energy ball mill made of rigid alloy material for ball-milling for 40 hours with the ball and material ratio at 20 : 1. The rotation speed of the ball mill is 200 rpm, and during the ball-milling, ethanol solution is added once every 5 to 6 hours to prevent oxidation and conglobation. After ball-milling, the powder undergoes acid washing with an acid mixture of nitric acid, phosphoric acid and water in the ratio of 1 : 1 : 5, and then is filtered through suction and drying. Samples of powder before and after acid washing are respectively taken for observation under transmission electron microscope. It is discovered that the powder before acid washing is not even, and large particles are around 0.2 microns in diameter, as shown in Figure 2: Transmission electron micrograph for powder before acid washing. The powder after acid washing is highly even, and the average particle diameter is around 50 nanometers, as shown in Figure 3: Transmission electron micrograph for powder after acid washing. The nitrogen gas adsorption method is used to measure the specific surface area for powder before and after acid washing, which is then converted into the average particle diameter of the powder d_{BET}. The results are: d_{BET} = 147 nm for powder before acid washing, and d_{BET} = 53 nm for powder after acid washing.

Implementation Case 2: 100 grams of the same ball-milled sample is taken, treated with cleanup acid treatment in an acid solution of hydrochloric acid : water = 1 : 5, and filtered through suction and drying. Nitrogen gas adsorption method is used to

measure the specific surface area for powder before and after acid washing, which is then converted into the average particle diameter of the powder d_{BET}. The results are: d_{BET} = 151 nm for powder before acid washing, and d_{BET} = 46 nm for powder after acid washing.

Attached Drawings for the Description

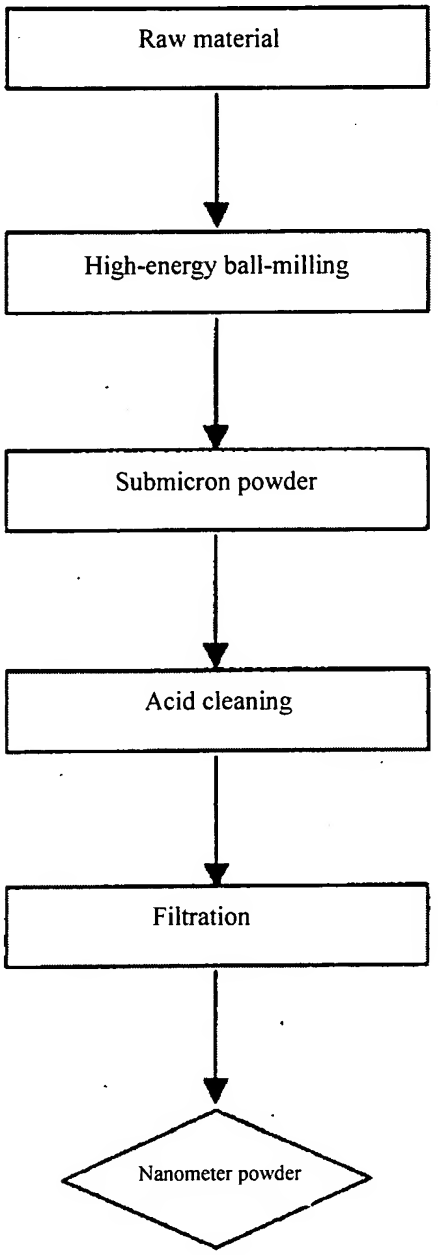

Figure 1

Attached Drawings for the Description

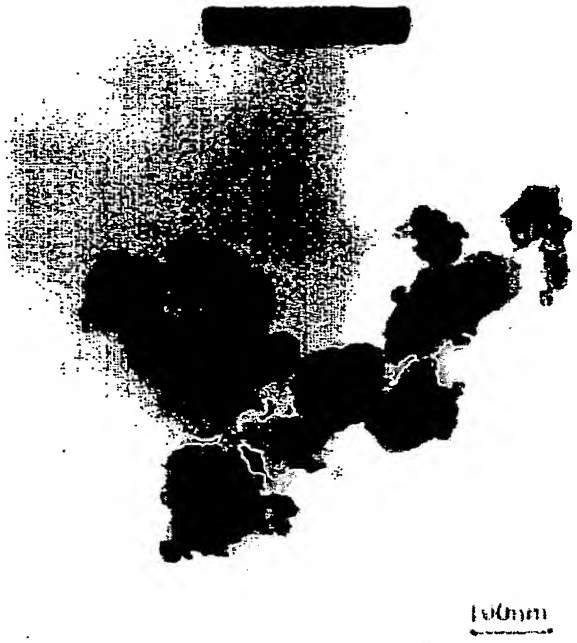

Figure 2

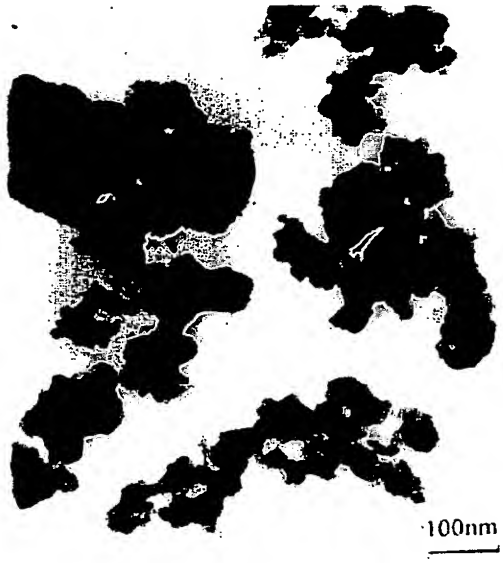

Figure 3

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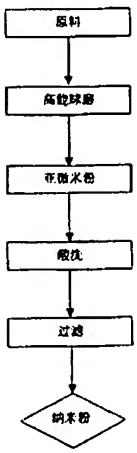
权利要求书1页 说明书3页 附图页数2页

[54]发明名称 二硼化钛纳米粉的制备方法

[57]摘要

本发明涉及二硼化钛纳米粉的制备方法。本发明首先将平均粒径为5微米的二硼化钛粉末进行球磨，提供颗粒表面一定的活化能和晶内缺陷，得到亚微米级粒径不均的二硼化钛粉；随后在酸性溶液中对粉末进行二次细化和均匀化处理，经酸洗处理后即可得到平均粒径为50纳米左右的二硼化钛纳米粉。本发明的优点在于工艺简单，粉末粒径均匀，适宜大规模制备粉体。



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权 利 要 求 书

1. 一种二硼化钛纳米粉的制备方法，其特征是将平均粒径为 5um 的 TiB_2 粉末进行高能球磨处理，球料比为 20：1，球磨 40~50 小时，获得粒径为 0.1~0.3um 的粉体，将此粉末置于浓盐酸与水混合的酸性溶液或浓硝酸、浓磷酸与水混合的酸性溶液中，搅拌 30 分钟后，在室温下静置 10 分钟，用水清洗 2~3 次，抽滤，烘干，即得到平均粒径为 50nm 左右的、均匀的 TiB_2 纳米粉体。
2. 按照权利要求 1 所述的制备方法，其特征是用于酸洗的酸性溶液的配比为：浓盐酸与水的比例为 1：5~1：8，或者浓硝酸：浓磷酸：水的比例为 1：1：3~1：1：5。

说　明　书

二硼化钛纳米粉的制备方法

技术领域

本发明涉及纳米粉的制备方法。

背景技术

二硼化钛（TiB_2）陶瓷粉料是一类重要的工程陶瓷原料，具有高熔点、高硬度、高化学稳定性以及良好的导热、导电性能。主要应用于：硬质工具材料、高温耐腐蚀电极、大规模集成电路用高强度引线框架材料等。目前应用较多的二硼化钛陶瓷粉料是利用自蔓延高温合成技术制备的，其平均粒径约 5um。为了进一步提高材料性能，需要制备纳米级硼化钛粉料。1995 年，美国 Washington University 的 Susan E. Bates 在期刊《Journal of Material Research》中发表了名为“Synthesis of titanium boride nanocrystallites by solution-phase processing ”的论文，用 $NaBH_4$ 和 $TiCl_4$ 为原料，在三甲苯溶液中，164℃下反应合成无定形的 TiB_2 先驱粉，然后在 900~1100℃下退火，制得粒径范围 5~100nm 的 TiB_2 纳米粉。这种制备技术工艺复杂，产物成分难以控制，需要进行后处理，不易实现大批量的工业生产。 1996 年，《Journal of Material Research》又发表了 Washington University 的 R.L.Axelbam 的论文“Gas-phase combustion synthesis of titanium boride nanocrystallites”，报道了采用 $TiCl_4$、BCl_3、Na 为原料，通过 Na 气气氛中的气相燃烧反应，制备出了粒径小于 15nm 的 TiB_2 纳米粉末。此技术可以制备出粒径小、纯度较高的 TiB_2 纳米粉，但其要求的技术含量及成本都比较高。

目前纳米粉的制备技术主要包括：化学气相法，化学共沉淀法，机械合金化法，溶胶-凝胶法，喷雾热解法及流态化法等。化学气相法工艺条件要求严格，成本较高；化学共沉淀法需要选择能够在碱性溶液中溶解的前驱体，对制备硼化物难度较大；机械合金化法制备的纳米粉粒径不均匀；溶胶-凝胶法原料价格高、有机溶剂具有毒性，同时在高温下作热处理时易使颗粒快速团聚；喷雾法需要高温及真空条件，对设备和操作要求较高；流

态化法工艺及设备复杂，大批量制备成本高。

发明内容

本发明的目的是：利用一种比较简易的方法，大批量制备出粒径均匀的 TiB_2 纳米粉。

本发明解决其技术问题所采用的技术方案是：（1）针对微米级的 TiB_2 粉料，利用机械化学方法初次细化晶粒，得到粒度不均的亚微米级粉体，同时产生一定程度的晶格畸变，活化颗粒表面；（2）通过酸洗处理进一步细化晶粒，利用硼化物的层状结构及吸氢性，获得粒径均匀的纳米 TiB_2 粉。

本发明的具体实现过程详述如下：

1. 将平均粒径为 5um 的纯度 98%以上 TiB_2 粉末进行高能球磨处理，球料比 20:1，球磨 40~50 小时。获得粒径 0.1~0.3um 的粉体。
2. 将浓盐酸与水按 1：5~1：8、或浓硝酸、磷酸和水按 1：1：3~1：1：5 制成酸性溶液，将球磨处理的粉末放入上述酸性溶液中搅拌 30 分钟，在室温下静置 10 分钟后，用水清洗 2~3 次，以去除沉淀物表面的酸性物质，抽滤，烘干，即得到粒径为 50nm 左右的、均匀的、纯度 98%以上的 TiB_2 纳米粉体，

本发明的优点在于：与其它纳米粉制备技术相比，工艺简单，粒径均匀，易于进行大批量制备。

具体实施方案

下面结合附图详细介绍本发明的具体实施方案。

图 1：二硼化钛纳米粉的制备工艺流程图。

实例 1：100 克平均粒径为 5 微米的 TiB_2 粉末，与适量无水乙醇混合，置于硬质合金材质的高能球磨机中球磨 40 小时，球料比 20:1。球磨机转速为 200 转/分钟，球磨时每隔 5~6 小时加入一次乙醇溶液，以防止氧化和团聚。球磨后的粉末用硝酸：磷酸：水=1：1：5 的混合酸进行酸洗，抽滤，烘干。取酸洗前后的粉末样品在透射电子显微镜下进行观察，发现酸洗前粉末不均匀，大颗粒在 0.2 微米左右，如图 2：酸洗前粉末的透射电镜图所示。酸洗后的粉末很均匀，平均粒径 50 纳米左右，如图 3：酸洗后粉末的透射电镜图所示。利用氮气吸附方法测定酸洗前后粉末的比表面积，再换算成粉末的平均粒径 d_{BET}. 结果为：酸洗前的粉末 d_{BET}=147nm，酸洗后的粉末 d_{BET}=53nm。

实例 2：取 100 克同样球磨处理的样品，在盐酸：水=1：5 的酸性溶液中进行酸洗处

理，随后抽滤，烘干。利用氮气吸附方法测定酸洗前后粉末的比表面积，再换算成粉末的平均粒径 d_{BET}. 结果为：酸洗前的粉末 d_{BET}=151nm，酸洗后的粉末 d_{BET}=46nm。

说 明 书 附 图

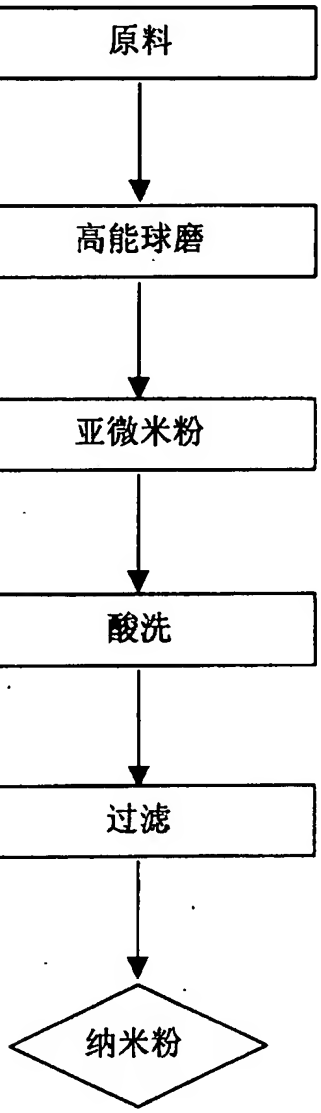

图 1

说 明 书 附 图

图 2

图 3

TRANSPERFECT
TRANSLATIONS

THE LEADER IN INTERNATIONAL COMMUNICATIONS

Affidavit of Accuracy

This is to certify the following document: Application No.: 02115664. 6, has been translated from Chinese into English by staff members of TransPerfect Translations familiar with both the Chinese and English languages and is to the best of our knowledge, ability and belief, true and accurate translation.

Leigh Wellman

Leigh Wellman
For TransPerfect Translations

Sworn to before me this
Friday, November 17, 2006

Susan Christian

Signature, Notary Public